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FINAL REPORT

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EXHAUST GASES FROM ENGINES HAVING SPECIAL CONTROLS

by

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ABSTRACT

Aliphatic and aromatic hydrocarbons containing from one through ten carbon atoms were identified in automotive engine exhaust by use of gas chromatographic techniques. Quantitative comparisons were made with the engine operating under varying conditions of load, fuel mixture and combustion. A heated tube connecting the engine exhaust to the chromatograph was used to facilitate direct analysis. Conventional packed columns and large diameter Golay chromatographic columns which can be used in trace analysis were designed, constructed, and successfully applied to this work.

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I. INTRODUCTION

Automobile exhaust is recognized as a major factor in air pollution with its attendant health problems. However, because of the many variables involved--engine construction and operation characteristics, fuel compositions, atmospheric and solar radiation variables, to mention a few--the problems of correlation of exhaust composition with these variables are difficult.

This report covers a two-year study of these problems. During a portion of this period, a major contribution to control and measurement of the variables of engine construction and operation was available to this program in the form of an experimental engine of special design. Coupled with this was an analytical program combining the disciplines of chemistry, physics, and electronics in the design and development of equipment specially adapted to exhaust gas study.

The technique of standardization of a number of gas chromatography columns and the identification of characteristic exhaust hydrocarbons through C_{10} provided information which will be of use in further studies of this nature. Some analyses of engine exhausts are included in this report. Material failures during the mechanical experimental phase of engine operation prevented accumulation of the large volume of exhaust analysis data planned for this investigation. However, experimentation which continued during engine "down-time" included studies of apparent concentration changes in samples stored in Mylar bags and development of techniques for separation of aliphatic and aromatic hydrocarbon isomers boiling in the range of 80° to 180° C.

It is anticipated that these studies will open the way to further work which ultimately will lead to the clear identification of those components whose presence in automotive exhaust can be correlated specifically with engine construction and operation and that design modifications might be indicated for decreased production of those components which constitute health hazards.

II. EXPERIMENTAL EQUIPMENT

A. The Exhaust Producing Engine

The engine was a Falcon 6-cylinder, 100 hp, 170 cu in. engine with standard equipment. Modifications designed by the late Professor Robert L. Allen of the Georgia Tech School of Mechanical Engineering consisted of a fuel injection system and rotary valves designed to prevent back flow of the exhaust gases into the intake manifold during the period of valve overlap. The load was applied by a Taylor hydraulic dynamometer. The engine in Figure 1 is shown without modifications.

Samples were taken from the engine operating under the following conditions:

(1) Standard carburetor and ignition system in good adjustment (provisions are made for individual cylinder sampling).

(2) Fuel injection system using conventional intake and exhaust valves with injection and ignition timing adjusted for maximum efficiency.

(3) Fuel injection and rotary valves with the timing adjusted for maximum efficiency.

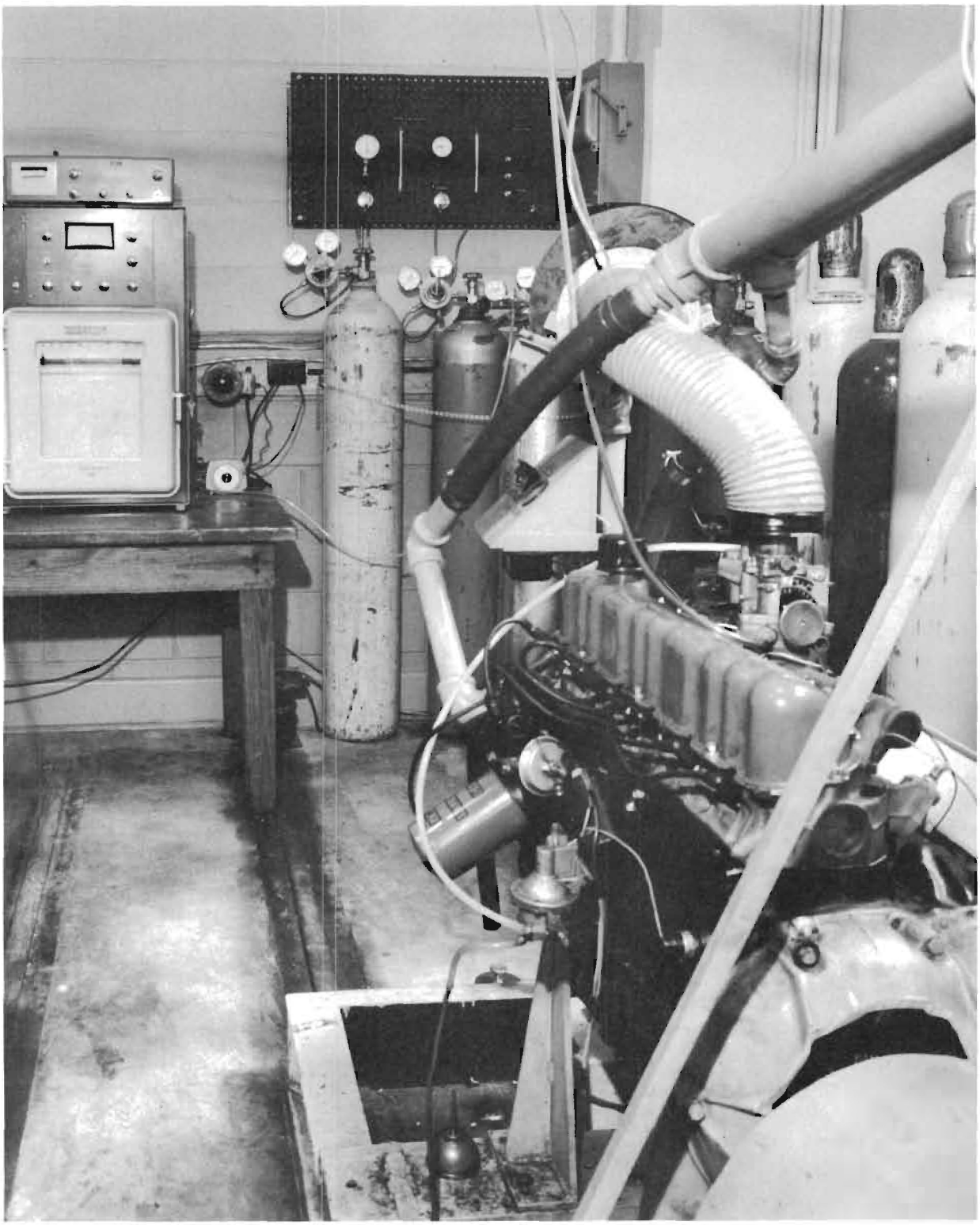


Figure 1. The Exhaust Producing Engine.

Engine variables recorded during each run to insure reproducibility were as follows: (a) revolutions per minute; (b) horse power delivered; (c) manifold pressure; (d) ignition spark advance; (e) exhaust port temperature; (f) air intake temperature; (g) cut off position of the rotary valves; (h) air intake rate; (i) fuel consumption rate; (j) room temperature (wet and dry bulb); and (k) atmospheric pressure.

The fuel used was Standard Oil Indolene motor fuel. This gasoline mixture remains constant throughout all seasons of the year.

B. The Gas Chromatographic Units

The instruments for this work were the Perkin-Elmer 154-D vapor fractometer and the Perkin-Elmer Model 810 gas chromatograph. Both units employ hydrogen flame ionization detectors and gas sampling valves. A separate Leeds and Northrup strip chart recorder with a sensitivity of 1-5 mv was provided for each instrument. The Model 810 is suitable for single or dual column operation and was modified for temperature programming. The gas chromatographic equipment is shown in Figure 2.

The units accomodate gas samples up to 25 ml and liquid samples via the heated injection port up to 10µl. The carrier gas is prepurified nitrogen and the detector gases are air and hydrogen.

The exhaust from the engine was conducted directly to the chromatographic units over a distance of 20 ft. via a heated stainless steel tube and introduced via gas sampling valves. Standard samples consisted of 10 ppm mixtures of the low boiling compounds and 100 ppm mixtures of the high boiling compounds, contained in gas cylinders or Mylar bags. For daily calibration a 10 ppm mixture of propane was stored in a prepurified nitrogen cylinder.

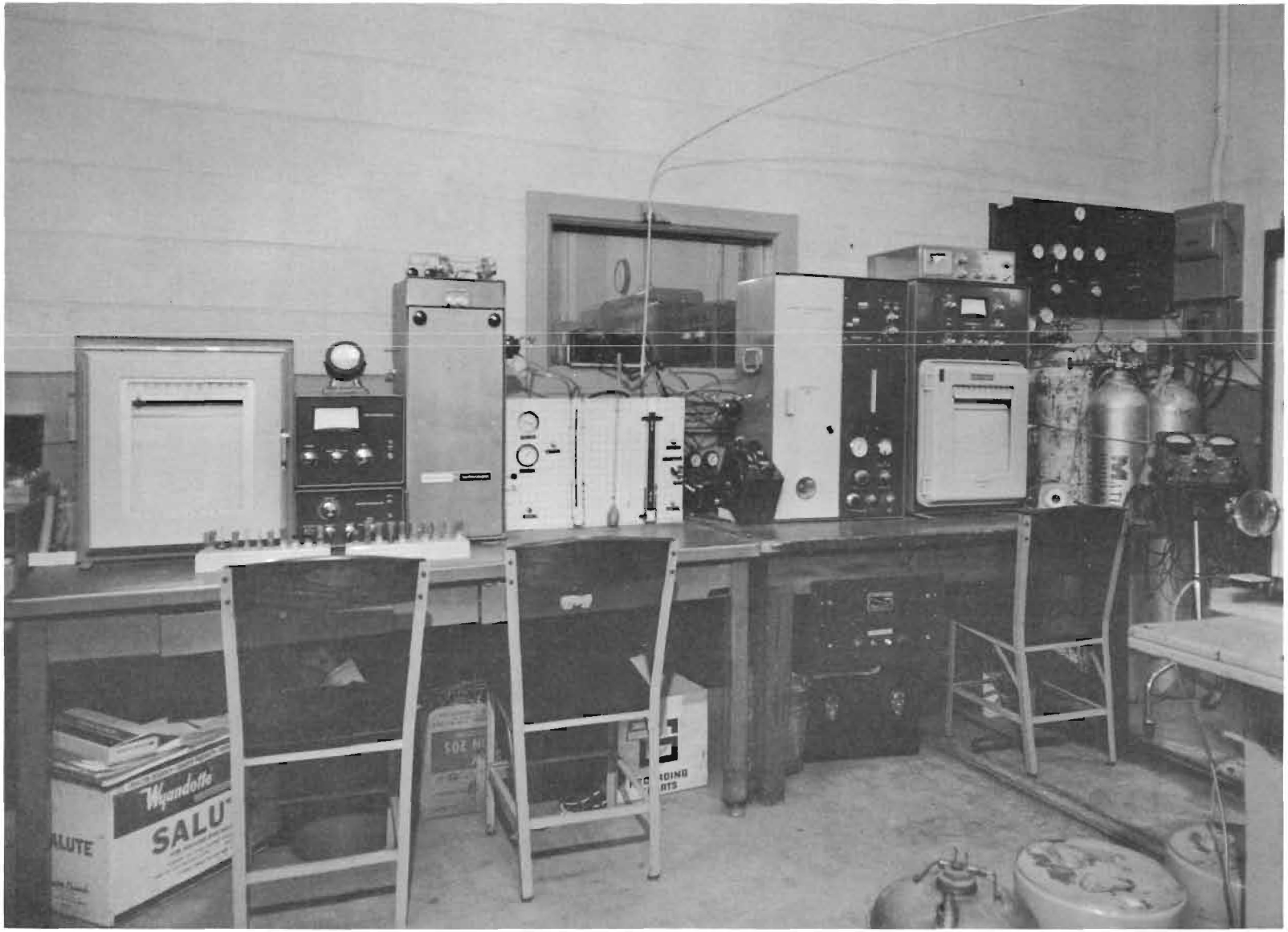


Figure 2. Gas Chromatography Laboratory.

C. Packed Chromatographic Columns

Packed columns were used more extensively in this work than Golay columns and served to identify paraffins through isopentane, olefins through 1-pentene, and aromatics through butyl benzene. About 85 per cent of the compounds ranging through 2,2,5-trimethyl hexane were identified using a combination of packed and Golay columns.

1. Gas-Solid Columns

Packed columns made of activated alumina, silica gel, and activated charcoal were used to identify compounds ranging from methane through isobutane. Adsorption columns have greater resolving power for the very low boiling compounds than the gas-liquid columns. However, because of variations in the adsorption characteristics, gas-solid chromatography is not as exact as gas-liquid chromatography 1/. Retention times are known to differ by as much as 100 per cent from day to day due to irreversible adsorption of exhaust compounds and water. However, this is of little significance as the number of isomers, and consequently, the chance of unresolved peaks and confused identity, is small for this range of carbon numbers. The results from an activated alumina separation are presented later in the report.

2. Gas-Liquid Columns (Packed)

Standard 1/8 and 1/4 inch O.D. copper tubing ranging in lengths from 3 to 20 ft. were used in making the columns. The solid support used was crushed and screened firebrick; i.e., Coast GC-22, John's Manville Chromosorb P, and Chromosorb W. The liquid compounds used were diisodecyl phthalate, di-2-ethylhexyl sebacate, didecyl phthalate, Union Carbide

carbowax 1500 and 1540, squalane, Ucon fluid LB-550-X, Dow Corning silicone oil 710, General Electric silicone fluid 96, dimethyl sulfalane, benzo (h) quinoline, Apiezon L grease, and m-bis (phenoxy phenoxy) benzene. Organic modified clays (Bentone 26, 34, and 38) on the support material performed the function of a liquid phase. Several columns composed of segments bearing different liquid phases and columns employing mixed liquid phases were examined.

3. Column Packing Procedure

The proper proportions of solid and liquid were determined by weight; the concentrations ranged from 5 to 25 per cent liquid with respect to total weight. Firebrick about 60 to 80 mesh was then combined with the liquid phase in a solvent of sufficient quantity to distribute the liquid phase evenly. A rotary evaporator was used to remove the solvent, and the firebrick was then dried for 24 hours in an oven at a temperature well below the boiling point of the liquid phase [2,3].

A 1/8 or 1/4 inch tube was filled with the coated firebrick by applying either pressure or vacuum together with vibration to cause the solid material to flow. Columns up to 6 ft in length were packed in this manner and these sections joined with Swagelock fittings if greater lengths were desired.

D. Golay Columns

The Golay column is an open tubular column in which the liquid phase is coated on the inside of the tube [4].

Much literature is available concerning chromatographic techniques using Golay columns of 0.010 to 0.03 inch ID [5,6,7] with efficiencies up to 750

plates per foot. Column lengths range from 100 to 1000 ft. Very little work has been reported using columns of larger diameter; however, the latter are much more desirable in work involving trace analysis. The volume of the conventional Golay columns is small; consequently, the column can separate only a small sample of gas. Approximately 1 μl of liquid hexane, which is then split at a ratio of 1:500, is a typical injection volume for a column of 0.010 inch diameter (i.e., 2×10^{-3} μl is introduced to the column) 8/.

Large diameter Golay columns up to 0.061 inch can accommodate 2 μl hexane 9/, about 3×10^{-3} gm. Thus, the larger diameter column can perform separations with sensitivity approximately 1000 times that of the smaller column.

Several large diameter Golay columns were prepared using squalane, Ucon fluid 550-X, and Dow Corning silicone fluid 710. The column length of 500 ft. was coated with the substrate by forcing a dilute solution of the substrate through the column. The solvent was then evaporated by passing a clean gas through the column. The squalane column yields 71,000 plates for the hexane peak and 13,000 for the octane peak. The number of plates is calculated from the formula, $n = \left(\frac{4T}{\Delta t}\right)^2$, where T = retention time, Δt = extrapolated peak width, and n is the number of theoretical plates. Large diameter Golay columns were found to be unsuitable for hydrocarbons boiling below 30° C unless the column is cooled below room temperature. It was found that the optimum separation occurs at about 75° C below the boiling point of the compound under analysis.

E. Gas Sampling Valve

Immediately after beginning this work it became obvious that the major problem was one of sampling; that is, the collection and analysis of exhaust gas samples without opportunity for chemical changes to occur. Oxidation, hydration, surface adsorption, and condensation are of considerable importance when the exhaust gas contains numerous hydrocarbons in a water saturated mixture.

A heated stainless steel tube was installed to conduct the exhaust gases from the exhaust manifold directly to the Perkin-Elmer gas sampling valve. Using the arrangement shown in Figure 3, reproducible samples were injected into the chromatographic column via the following technique:

In the "sample" position of the valve, the exhaust gases are pumped through the standard gas loop in a continuous stream. When equilibrium is reached, the valve is rotated counterclockwise to the "Inject" position. In this position the standard volume is in series with the carrier gas line. The sample is then swept into the column by the carrier gas.

By means of its own resistance to an ac current with a potential drop of approximately 10 volts, the stainless steel tube is heated to about 100° C. The temperature is proportional to the voltage, which is controlled by a Variac variable transformer and measured by thermocouples connected to a potentiometer. The voltage is maintained at a constant value by a sola transformer. A water manometer is used to measure the pressure drop across the gas sampling valve.

The samples are reproducible within $\pm$ 1 per cent if the gas flow, pressure and temperature are controlled. Standard injection volumes are available

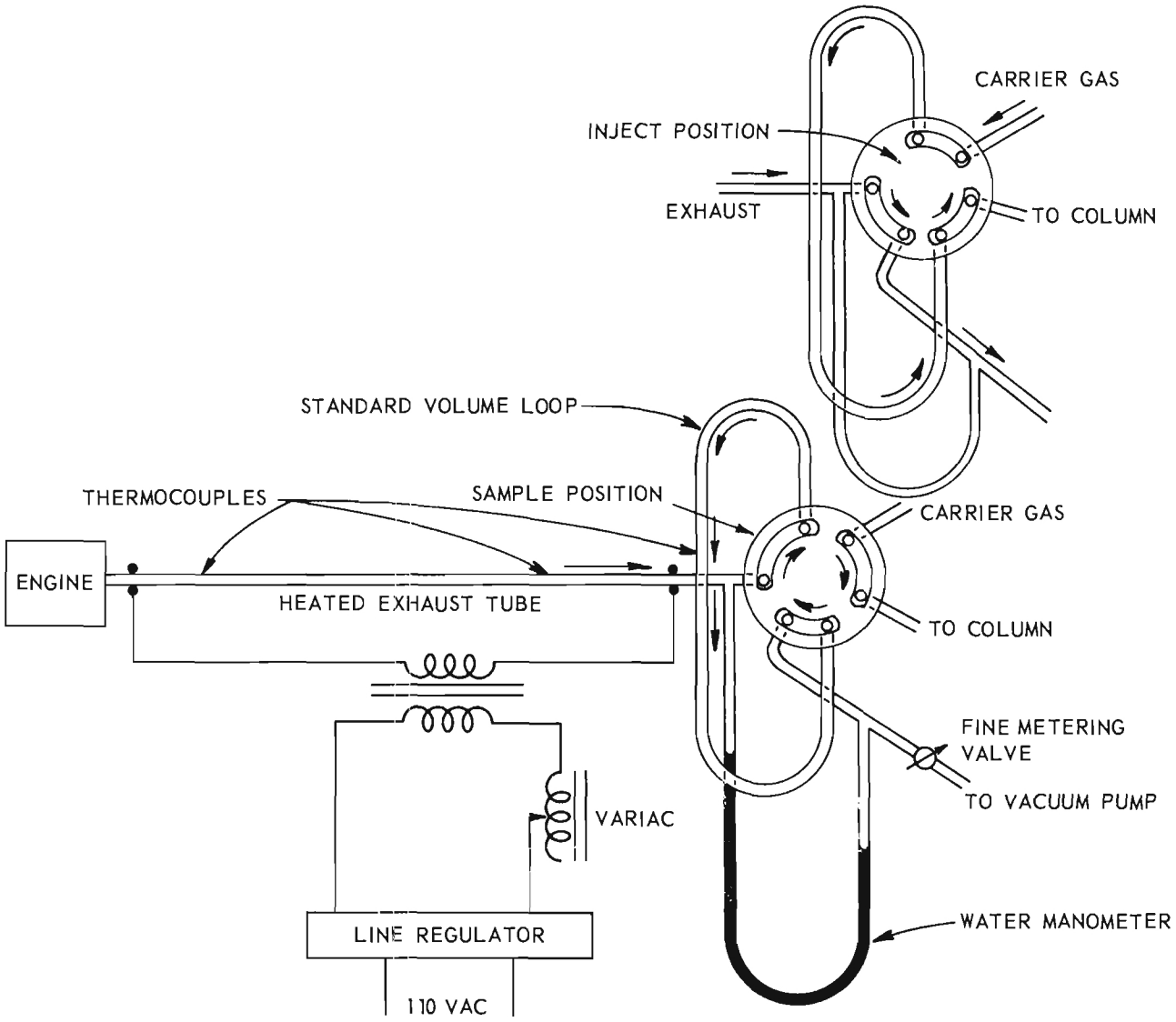


Figure 3. Schematic Diagram of Heated Exhaust Tube and Gas Sampling Valve.

for 1/4, 2, 5, and 25 cc. The exhaust tube and gas sampling valve are flushed periodically with a solvent to check for condensation of higher boiling compounds. No appreciable condensation has been observed.

F. Other Sampling Methods

1. Collecting by Condensation and Freezing

Samples were collected in small ampules by condensing the exhaust gases on dry ice or liquid nitrogen. With this method (see Figure 3), the vacuum pump and heated exhaust tube are not used. The ampule in which a sample is collected is placed inside the standard loop of the gas sampling valve, the sample is vaporized and the valve is rotated to the "Inject" position. For high boiling samples the valve should be placed in the "Inject" position for a given time, say 45 seconds, and then returned to the normal position.

This method is not desirable for accurate quantitative work because of selective condensation, which is known to vary with engine speed and humidity. The process is satisfactory for qualitative work, and the samples can be kept indefinitely if the ampules are sealed and stored on dry ice.

Injection of the condensed liquid by microliter syringe is not desirable if the liquid is a complex mixture containing water and hydrocarbons which boil over a wide range. Reproducibility was not obtained because some of the compounds are in the gaseous phase while the water is still frozen.

2. The Heated Gas Syringe

Exhaust gases collected in gas syringes yielded satisfactory results. The reproducibility of this method is exceeded only by the gas sampling valve method described previously. The syringe method is particularly useful if the exhaust producing engine must be located several hundred feet from the gas sampling valve. Samples are taken at exhaust temperature and injected as soon as possible. The syringe temperature, measured by a thermocouple, is maintained by a heating tape for a short period before the sample is injected.

There are three disadvantages which accompany the use of the gas syringe:

a) the amount of gas in the syringe is dependent upon the temperature of the syringe and setting of the plunger;

b) at high temperatures reaction can take place before injection; at low temperatures condensation is a problem; and

c) if a large sample is used the chromatographic efficiency is decreased due to the time required to push the syringe piston through the injection stroke. This causes sample spreading, which results in peaks of increased width. Column equilibrium is also disturbed when a large volume of gas is suddenly added to the system.

G. Mylar Bags as Containers for Gases

Altshuller and Clemens 10/ have described methods for using Mylar bags as containers for dilute mixtures of aromatic hydrocarbons of less than one part per million. This process has been enlarged to include almost all hydrocarbons in the low and medium boiling range.

1. Bag Construction

The bags are constructed from Type C Mylar of 1 mil thickness. A heat seal adhesive tape is used as the sealing agent.

The volume of the gas bag can be determined by a wet test meter 10/; however, it is more convenient to construct the bag in the shape of a rectangular solid. The volume is easily calculated from the measurements of the rectangular sides. The bag is constructed so that it fits snugly into a rigid box which prevents the bag from bulging when it is filled with gas.

2. Sample Preparation

The weight of nitrogen and hydrocarbons can be calculated from the sample volume corrected to standard conditions. The sample of liquid or gas is introduced into the system as follows:

(a) Trace quantities of the hydrocarbons are introduced into the chamber up stream from the bag (see Figure 4). Hydrocarbons can be introduced either in the liquid form via a Hamilton microliter syringe or by a multi-step dilution procedure. Gas and liquid densities are always corrected to standard conditions.

(b) After injection of the liquid, the evaporation chamber is heated over a hot plate to a prescribed temperature. When the sample is vaporized, prepurified nitrogen is passed through the chamber into an evacuated bag. The nitrogen carries the vaporized hydrocarbons into the bag, thus forming a dilute mixture of hydrocarbons in nitrogen. Gaseous samples are injected in the same manner (without heat) using a Hamilton gas syringe.

(c) Samples from the Mylar bag are introduced into the gas chromatograph by a gas sampling valve (see Figure 5).

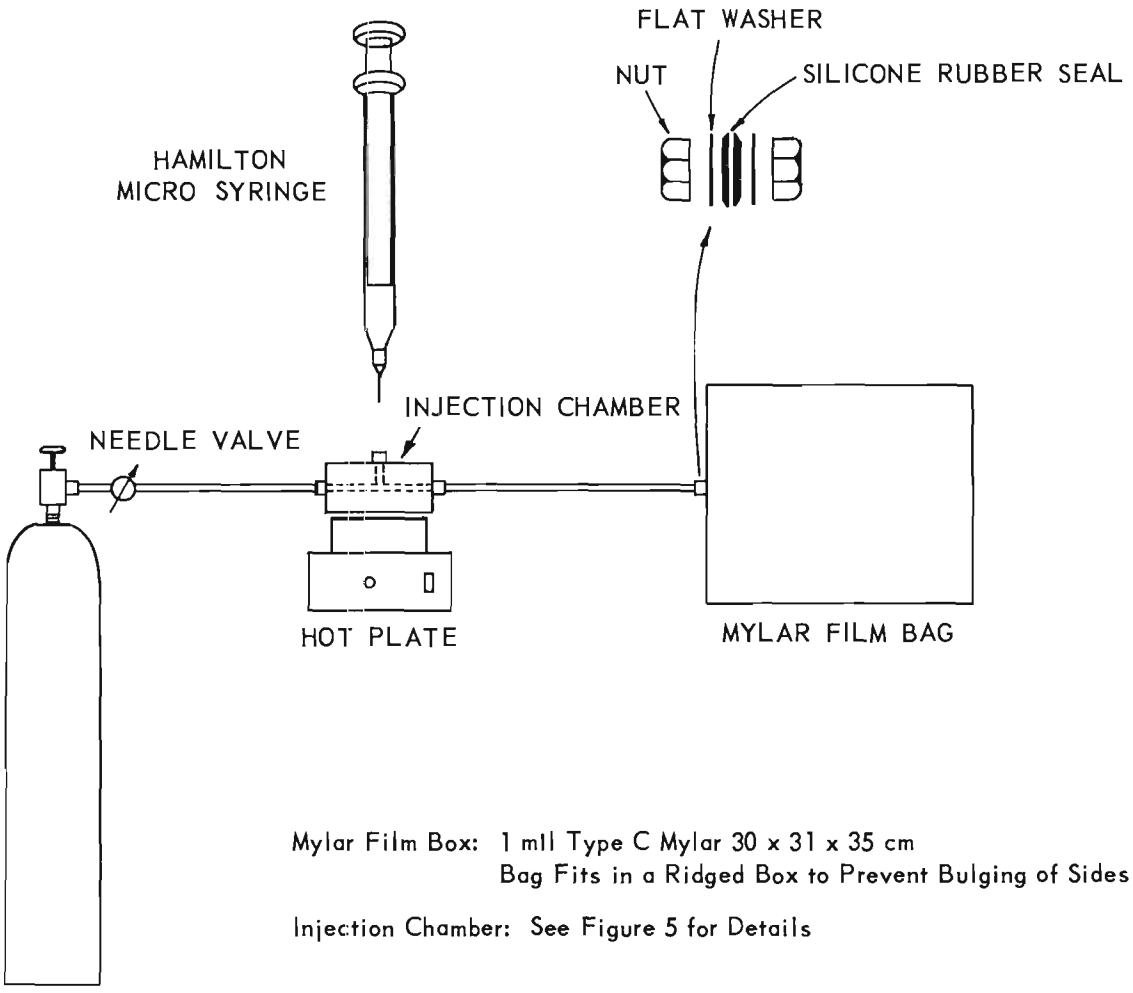


Figure 4. Mylar Bag Inflation System.

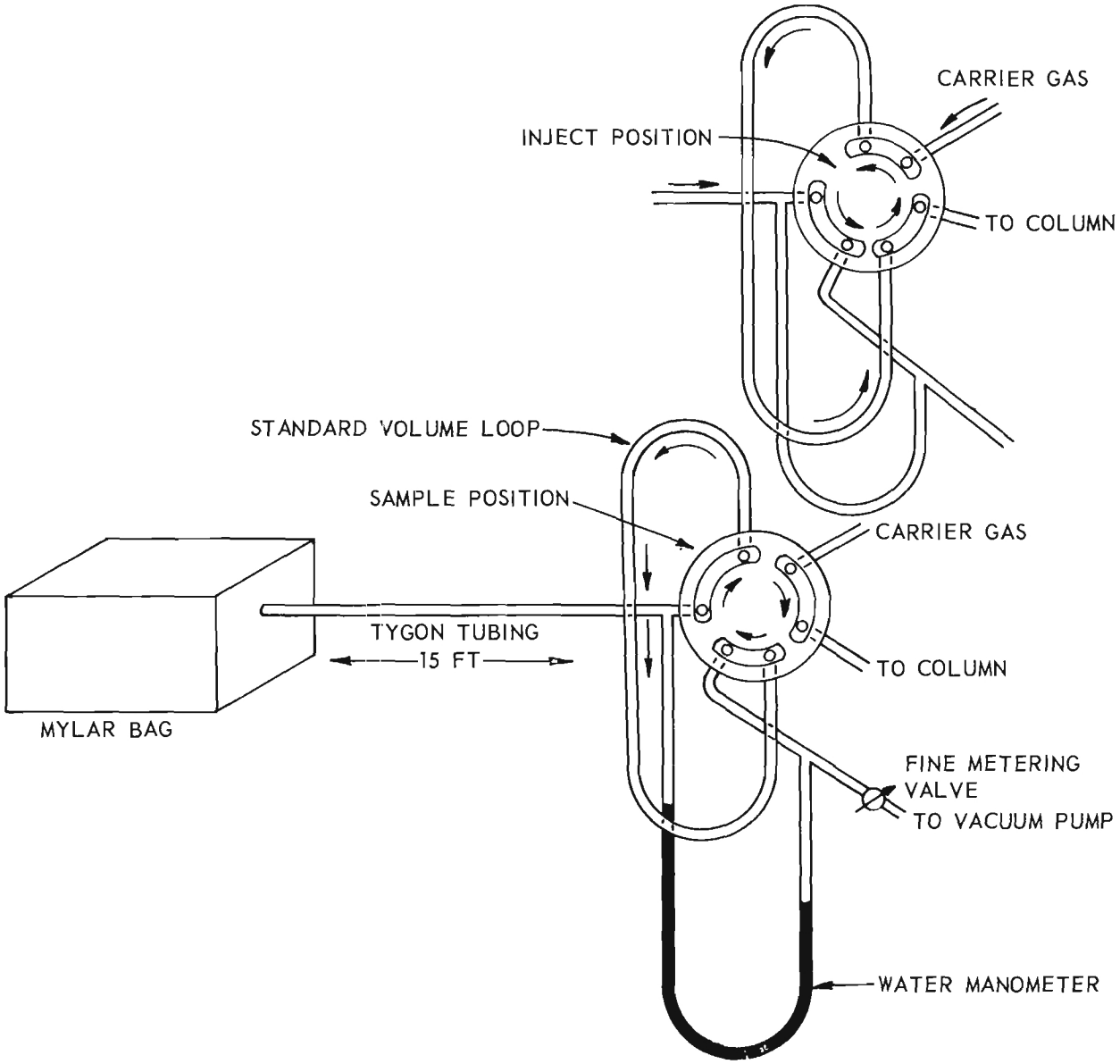


Figure 5. Mylar Bag Injection Method.

With the sampling valve in normal position, the metering valve is adjusted to give a flow of approximately 50 cc/min. A water manometer is used to insure reproducible flow rates. When equilibrium is reached, the sampling valve is rotated to the "Inject" position for a given time and then returned to standard position.

H. Gas Cylinders as Containers for Dilute Gas Mixtures

Standard 27 and 275 cu ft nitrogen cylinders were used to store dilute mixtures of hydrocarbons over long periods of time. Complex mixtures of eight to ten hydrocarbons from one to four carbons were prepared and used to standardize the detector.

1. Cylinder Preparation

A clean nitrogen cylinder at atmospheric pressure is connected to a larger cylinder of prepurified nitrogen. An injection block with a silicone rubber septum is placed in the line between the two cylinders as shown in Figure 6. With the metering valve closed and valve "B" open, a calculated volume of each hydrocarbon is injected through the septum. Hydrocarbon weight is computed from ideal gas laws using volume-density calculations taking room temperature and pressure into consideration. When the necessary weight has been injected into the chamber (see Figure 7) pressure screw "D" is inserted to hold the rubber septum in place at high pressures. Valve "A" is then opened and the system is slowly brought up to 1000-1500 psig. The weight of nitrogen can be calculated from the gage pressure using gas law calculations. As a check, the cylinder is also weighed on a Toledo hydraulic balance before and after filling.

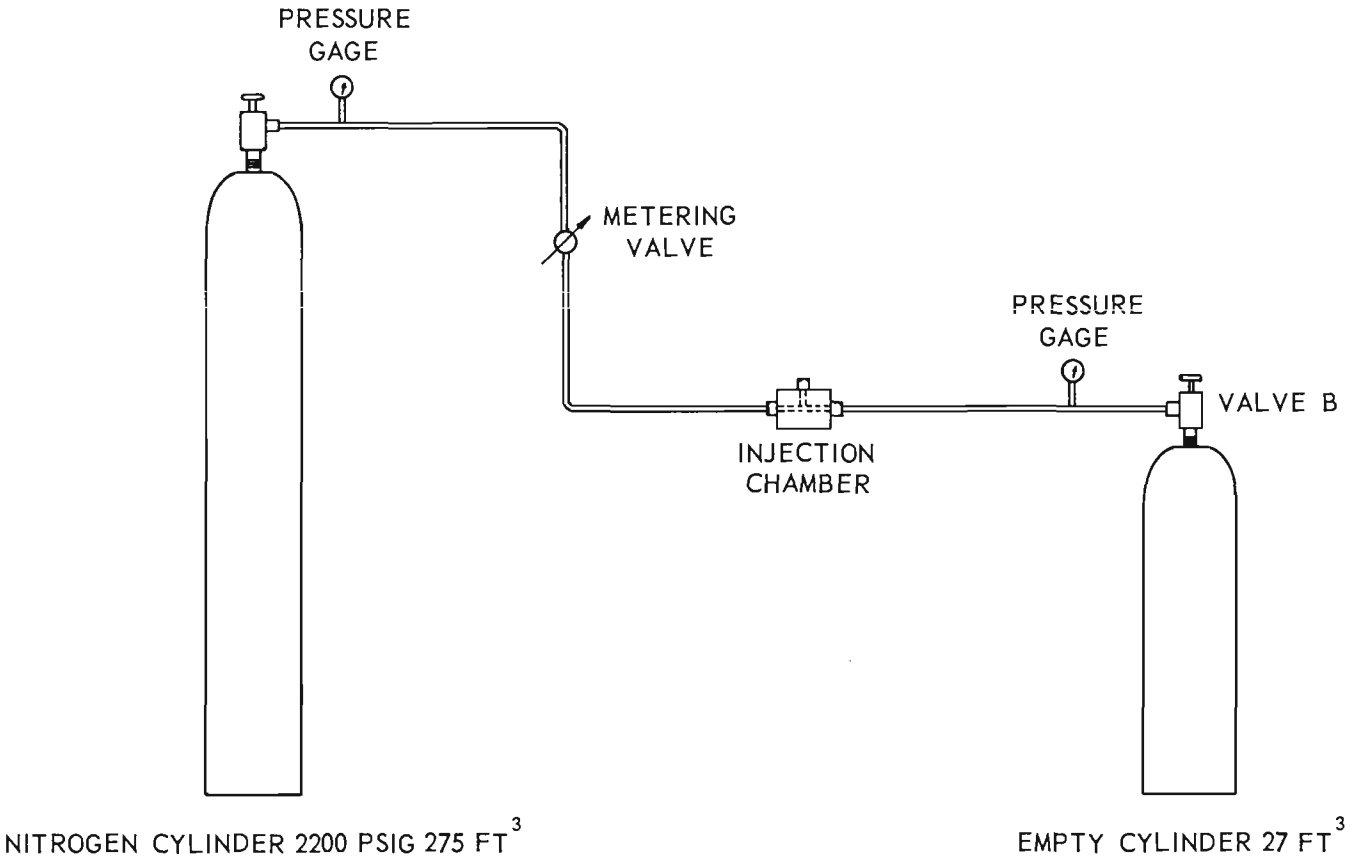
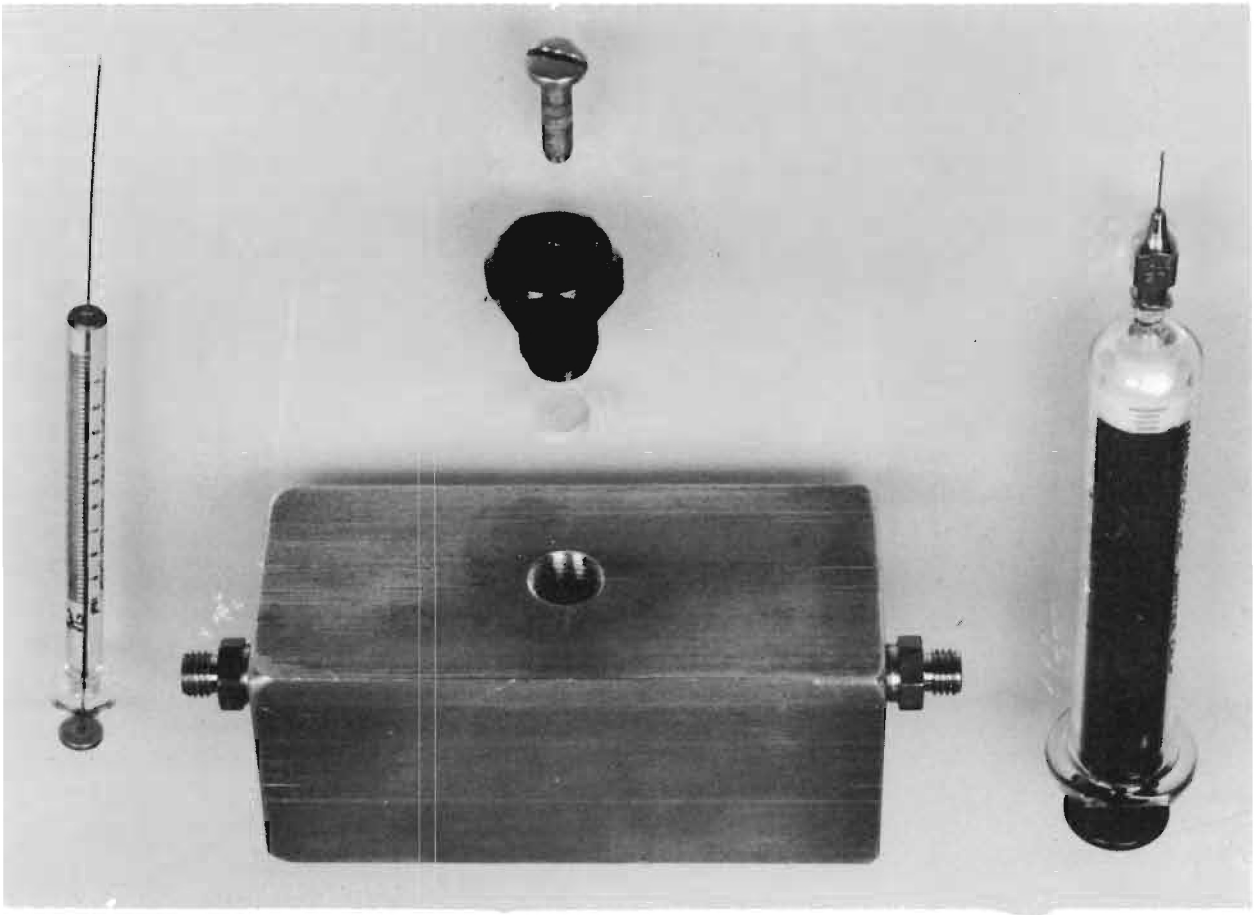


Figure 6. Injection Chamber and Nitrogen Pressure System.



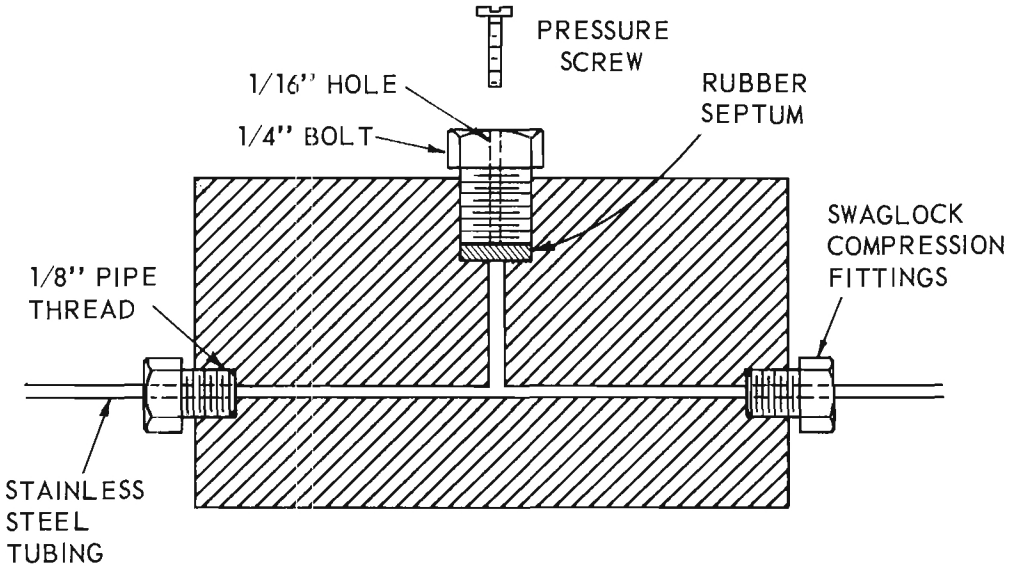


Figure 7. Injection Chamber.

2. Sample Introduction

The flame ionization detector is standardized using complex mixtures of dilute hydrocarbons in a process involving the previously mentioned Mylar bag and the gas cylinder.

A small Mylar bag is connected to a T-fitting on the tube leading from the gas sampling valve to the cylinder (see Figure 8). The bag is filled before each standardization so that effects due to surface adsorption of the Mylar are negligible.

The gas cylinder and Mylar bag combination serves as the qualitative and quantitative standard for the exhaust analysis for all compounds through C_4.

3. Aging Characteristics of Dilute Gases

Dilute gases stored in Mylar bags are known to decrease in concentration. This effect is probably due to surface adsorption of the Mylar. Figure 9 illustrates this aging effect with respect to time. There is some indication that the decrease in concentration is due to chemical change because the same results were observed for a Mylar bag which had been previously saturated with an identical mixture.

Equal weights of the following gases were diluted to 10 ppm in nitrogen: methane, ethane, ethylene, propane, propylene, isobutane, n-butane, 1-butane, and isobutylene. This mixture was used to determine the aging characteristics over a period of 10 days. All of the compounds do not vary by the same amount. Figure 9 represents an average variation of the C_1-C_4 mixture, as deviations were not constant but varied less than 0.5 ppm.

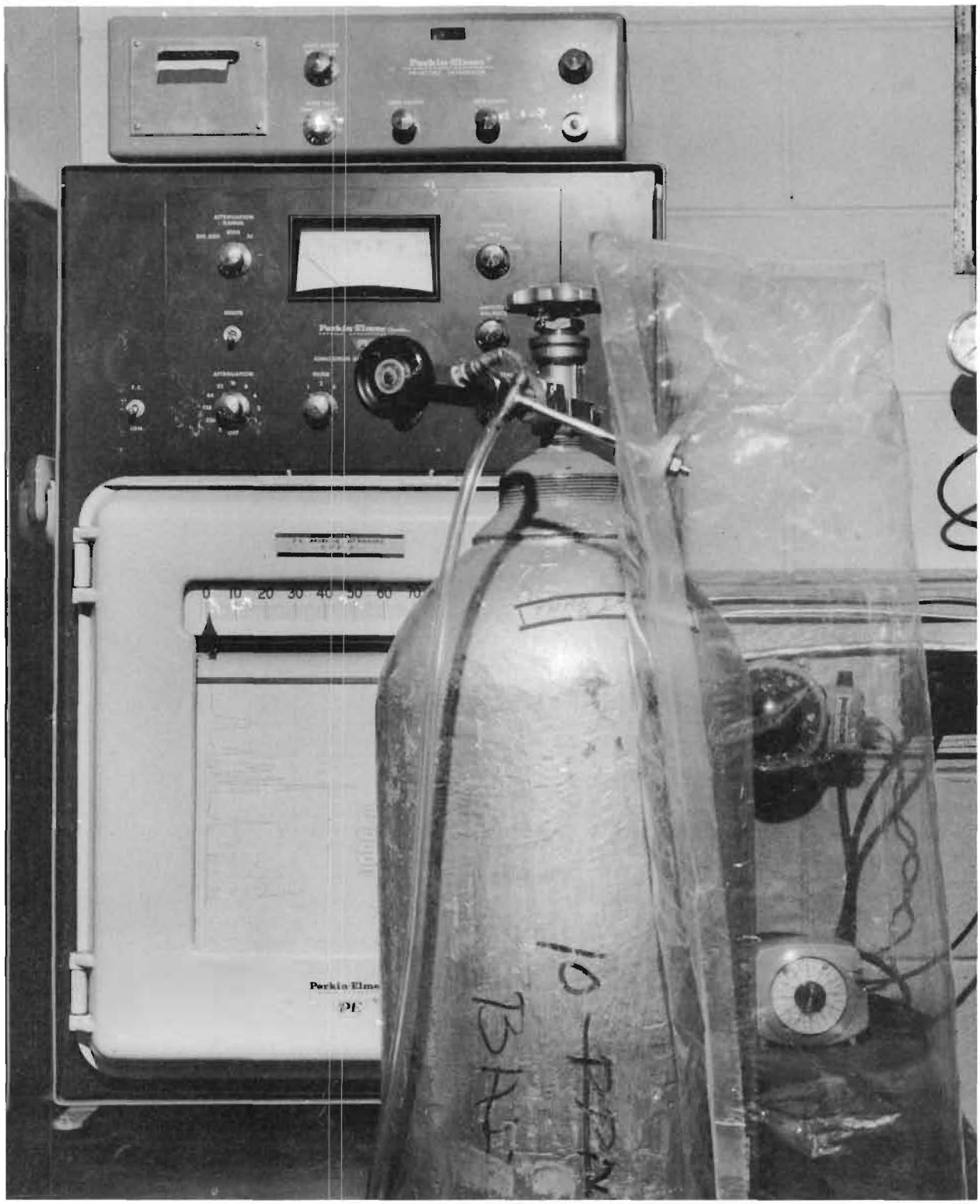


Figure 8. Gas Cylinder and Bag Combination.

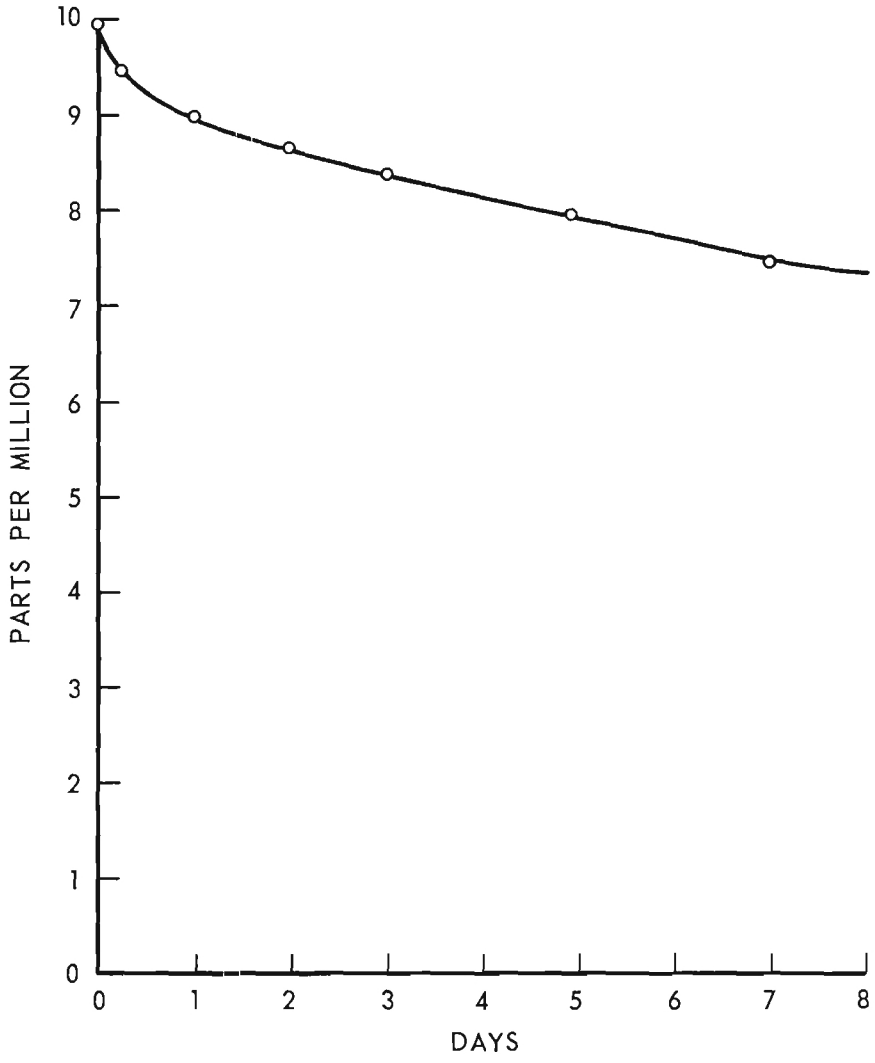


Figure 9. Aging Characteristics of Dilute Gases.

I. Liquid Standard Samples

The detectable concentration of medium boiling hydrocarbon samples stored in Mylar bags generally decreased with time, but exhibited comparatively wide day by day deviations. These deviations could not be correlated with any measurable experimental condition, e.g., wet or dry bulb temperatures, barometric pressure, or apparatus variables indicated by the 10 ppm propane standard. An alternative method of preparing quantitative and qualitative samples of these materials was required.

Of the alternate methods examined, preparation of dilute high boiling hydrocarbon solutions in a low boiling solvent, e.g., 5 μl of aromatics and aliphatic hydrocarbons of carbon number greater than C_8 in 5 ml research grade 2,4-dimethyl pentane gave reproducible retention times and peak areas over a period of several weeks. Medium boiling compounds of carbon number from C_5 to C_8 were similarly treated using toluene as the solvent. Injection of 0.2 μl dilute samples using a microliter syringe gave peak areas comparable to those obtained from the corresponding components in the exhaust samples. The principal handicap of this method was the long retention time for toluene under experimental conditions suitable for separation of lower boiling components.

J. The Flame Ionization Detector

The Perkin-Elmer flame ionization detector was observed to have an efficiency up to 10^{-8} gm of hexane with good signal-to-noise ratio. This is within the practical range since most exhaust concentrations are greater than 1.0 ppm per hydrocarbon.

The sensitivity of the flame detector is dependent upon the air, hydrogen, and carrier flow rates. The hydrogen and air are usually varied to achieve maximum sensitivity for a particular column separation. The graphs in Figures 10 and 11 illustrate the response of the detector in the Perkin-Elmer 154D due to changes in hydrogen and air flow with the carrier rate held constant. The flow rates are controlled by varying the pressure across the fixed restriction from 0 to 35 psig. While actual flow rates are not measured constantly, the pressure is indicative of the operation conditions and is held at a constant value by a two-stage and a single-stage regulator in each line. The hydrogen flow rate is approximately 30 ml/min, and the air rate is about 250 ml/min. The flow is varied $\pm$ 5 per cent to achieve maximum sensitivity for a particular carrier rate.

The detector in the Perkin-Elmer Model 810 gas chromatograph is a dual flame unit. Separate gas pressure and flow controls are provided for each flame. The properties of either flame in the detector, when operated as a single column instrument, are similar to those described above for the Model 154D. With both flames ignited, however, sensitivity of the detector is only about 1/10 of that obtained with single flame operation, and flame stability is greatly reduced as the single flame ionization detector is sensitive to oven temperature. These characteristics of dual flame operation in the instrument sharply restricted the use of temperature programming in this study.

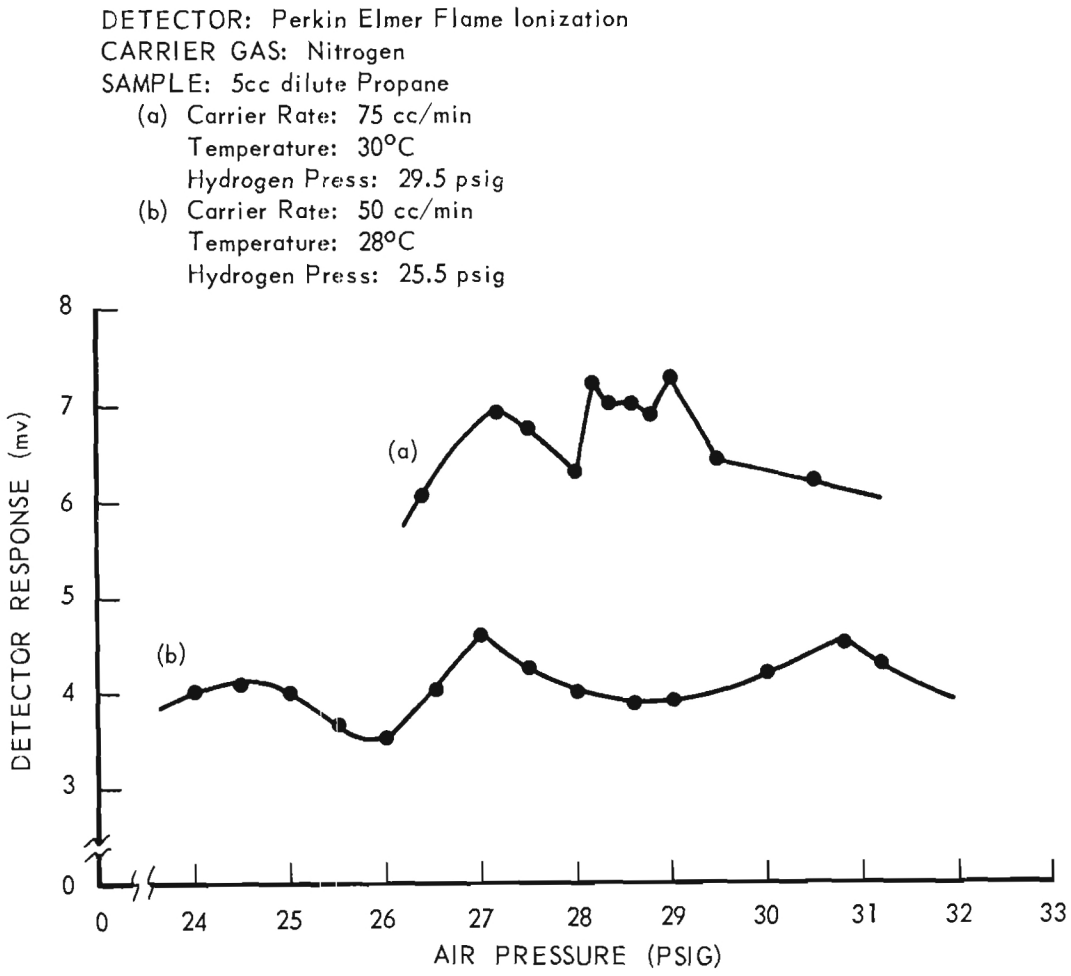


Figure 10. Air Pressure vs. Detector Response.

DETECTOR: Perkin Elmer Flame Ionization
CARRIER GAS: Nitrogen
SAMPLE: 5 cc dilute Propane
(a) Carrier Rate: 75 cc/min
Temperature: 30°C
Air Pressure: 28.5 psig
(b) Carrier Rate: 50 cc/min
Temperature: 31°C
Air Pressure: 27.0 psig

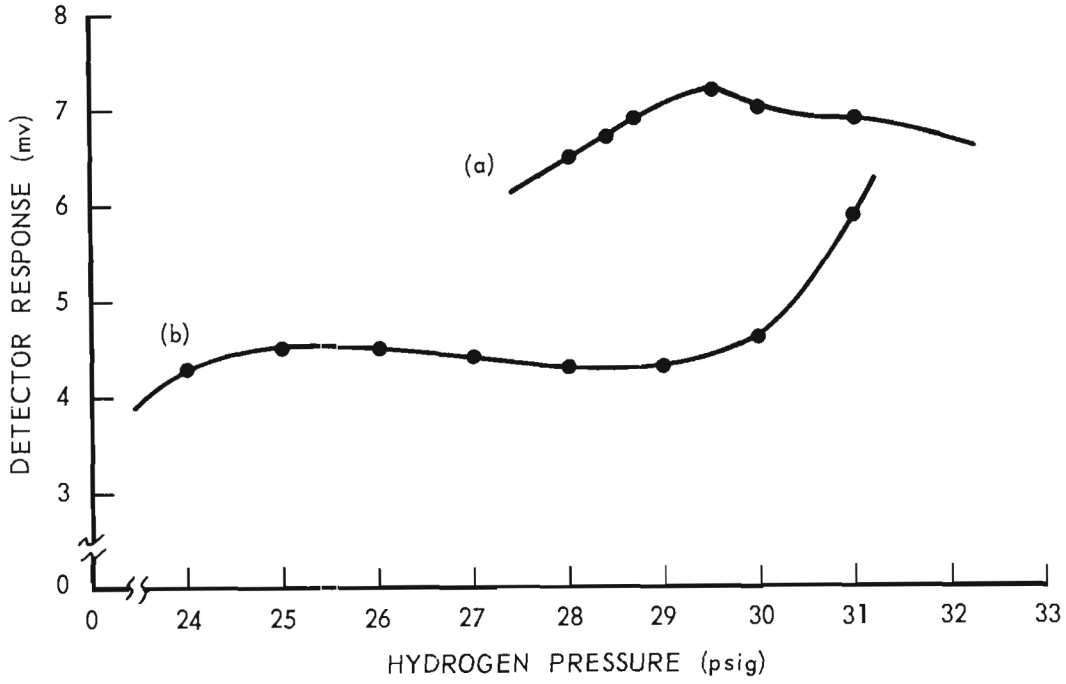


Figure 11. Hydrogen Pressure vs. Detector Response.

III. ANALYTICAL METHODS

A. Detector Response

The response of the hydrogen flame detector is linear for small quantities of hydrocarbons 3b/ up to about 10^{-4} µl. Knox 11/ indicates that the detector is linear for concentrations up to 0.5 per cent. According to Littlewood 2b/, there is no relation to molecular structure and the response of the flame ionization. Roughly, the response is directly proportional to the number of carbon atoms per unit weight of the sample; however, there are exceptions to this rule. For example, the molar response of 2,2,4-trimethylpentane is 30 per cent greater than that of ethylbenzene. The chromatograph must therefore be calibrated quantitatively as well as qualitatively for each compound which is to be analyzed.

B. Quantitative Standardization

The previously mentioned dilute hydrocarbon mixtures are used in quantitative and qualitative standardization of the instrument. The standard is prepared so that its concentration is of the same order of magnitude as the exhaust compound. Direct proportion can then be used to determine the concentration of the unknown. Thus,

$$\frac{A_s}{C_s} = \frac{A_u}{C_u}$$

where A_s = Peak area of the standard,

C_s = Concentration of the standard,

A_u = Peak area of the unknown,

C_u = Concentration of the unknown.

This equation assumes the following conditions:

(a) the volume of the standard equals the volume of the unknown;

(b) the detector response remains constant; and

(c) $C_s - C_u < 10^3$.

The area of narrow peaks is difficult to determine graphically. A formula was derived (see Appendix) which excludes peak width from the calculations.

C. Qualitative Standardization

A complete qualitative standardization is impossible because of the similarity of physical properties of compounds where the chemical nature is not similar. However, qualitative identification can be made provided that the following conditions 2c/ are met:

(a) the investigator has some foreknowledge of the nature of the complex mixture which would allow him to exclude certain compounds;

(b) several columns with different separation characteristics are available; and

(c) a large number of standard compounds are available which include all possible unknowns.

In this work, condition "a" is satisfied in that several sources indicate compounds which have been observed in automotive exhaust 12,13,14,15,16/ by gas chromatography and classical chemical methods. Condition "b" is satisfied through integrated use of gas-liquid separations by boiling point, gas-solid separations, and gas-liquid separations using columns which differ in polar activity. Reagent grade hydrocarbons, which are purchased from Phillips Petroleum Company and The Matheson Company, satisfy condition "c".

Identification techniques vary with the compound in question. For very low boiling hydrocarbons the process is rather straightforward because the number of isomers is small. The identification process increases in complexity with the increase in carbon atoms. For medium and high boiling hydrocarbons, several runs involving separation by boiling point, structure, and polarity are necessary.

During the second year of this study identification of components was facilitated by use of separate gas chromatographs for the lower and higher boiling fractions of the mixture. Separate samples from the engine test run were injected into each instrument by means of gas sampling valves over a time interval of less than one minute. Low boiling compounds were estimated using columns operated at 35°-75° C which separated compounds substantially in the order of increasing boiling point. Activated alumina, Dow Corning silicone oil 710 and dimethyl sulfalane columns were used for this separation. Higher boiling compounds, e.g., aromatics of carbon number greater than C-7 were separated at 100° C on a second column which exhibited selectivity for both boiling point and the orientation of aromatic substituents. Typical columns were Bentone 34 with diisodecylphthalate, Carbowax 1540, and m-bis (phenoxy phenoxy) benzene. Representative chromatograms are shown in Figures 13 and 15. Comparison of the two chromatograms was useful in determination of those components whose retention times are between those of benzene and toluene.

IV. EXPERIMENTAL DATA

A. The Low Boiling Hydrocarbons

1. Column Preparation

Table I lists ten hydrocarbons which were separated on a 1.5 meter alumina column. The alumina is 60-80 mesh which was prepared from Alcoa alumina F-6 by grinding with mortar and pestile and screening on U. S. Standard sieves. The slumina was deactivated by the addition of 1 per cent squalane 13/ which was applied as described in Section II-C-3.

2. Standardization

The composition of the standard mixture was established by trial and error. A suitable 10 ppm mixture was prepared in a 27 cu ft cylinder as described in Section G-2. This mixture and a 10 ppm propane-in-nitrogen cylinder served as the qualitative and quantitative standard throughout this phase of the work.

3. Results

The data of Table I show the results from the engine using fuel injection and rotary valves compared to a similar engine using a standard carburetor in good adjustment. The results are expressed in parts per million of the individual hydrocarbon in notrogen. Sample chromatograms comparing the fuel injection system to the standard engine are shown in Figure 12.

Values for isobutylene were obtained from a 4 meter dimethyl-sulfalane column at a temperature of -7° C. Erratic data resulted from the use of the

TABLE I

COMPARISON OF LOW BOILING EXHAUST COMPOUNDS

Compound	Results Expressed in Parts Per Million					
	1	2	3	4	5	6
Methane	90.5	17.8	18.5	10.2	61.3	337.0
Ethane	12.2	81.8	18.2	29.3	9.1	69.7
Ethylene	139.5	99.0	104.1	58.6	77.7	400.0
Propane	2.7	0.4	0.9	0.6	0.1	6.1
Acetylene	147.2	31.5	4.1	12.8	70.8	358.0
Propylene	159.4	103.2	123.5	98.6	61.6	131.4
Isobutane	3.1	0.5	0.1	0.1	4.2	34.6
n-Butane	54.9	28.5	25.5	25.0	0.1	73.4
1-Butene	36.4	29.4	--	27.3	0.1	56.0
Isobutylene	No Data----------					
Total	645.9	392.1	294.9	262.5	285.0	1162.9

1 - Falcon engine, fuel injection, rotary valves, 4.33 hp, 1000 rpm, 0.860 sp fuel consumption, 221 mm Hg manifold pressure, 12.6 air/fuel.

2 - Falcon engine, fuel injection, rotary valves, 3.8 hp, 625 rpm, 0.699 sp fuel consumption, 297 mm Hg manifold pressure, 14.9 air/fuel.

3 - Falcon engine, fuel injection, rotary valves, 37.3 hp, 1925 rpm, 0.459 sp fuel consumption, 622.5 mm Hg manifold pressure, 15.8 air/fuel.

4 - Falcon engine, fuel injection, rotary valves, 21.8 hp, 1625 rpm, 0.473 sp fuel consumption, 450 mm Hg manifold pressure, 16.33 air/fuel.

5 - VW engine,* standard equipment, 1000 rpm, no load.

6 - Falcon engine,* standard equipment, 1000 rpm, no load.

*This run was not a part of the present study.

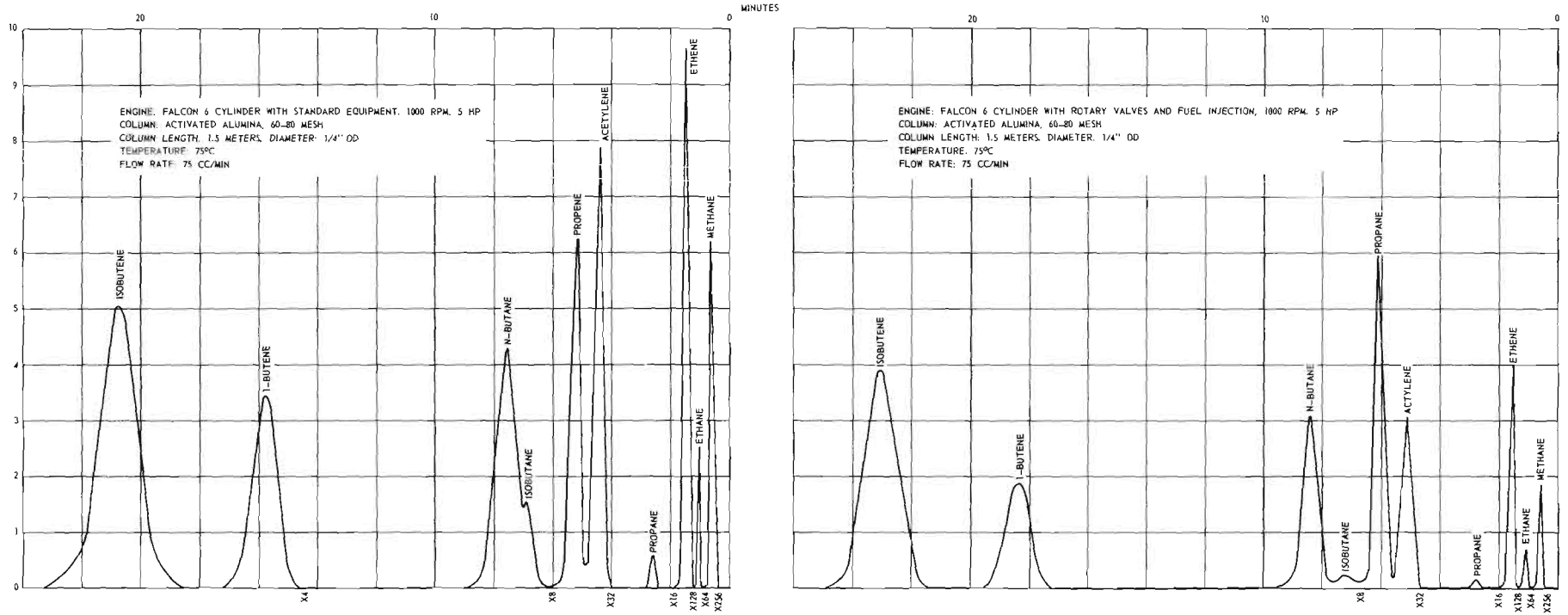


Figure 12. Gas Chromatograms of Low Boiling Compounds.

B. The Medium Boiling Hydrocarbons

1. Column preparation

Analyses have been obtained with the following packed columns: Silicone fluid 710, squalane, dimethyl sulfalane, Carbowax 1500 and Carbowax 1540. The columns were prepared as described in Section C-2 of this report. A 500 ft Golay column was also used.

2. Standardization

The detector response was standardized by using dilute vapors of hydrocarbons in Mylar bags.

3. Results

The exhaust components from the standard carburetor engine are indicated in Figures 13 and 14. The chromatograms shown represent a wide range separation. The unresolved peaks were resolved using more efficient columns over a narrow range of boiling points. Peaks identified as fuel components are known to exist in the gasoline but are not yet identified.

Exhausts from the experimental engine operated in several configurations and under a variety of speed load and fuel mixture conditions were analyzed using a 6 meter 1/4" O.D. column packed with 10% Dow Corning 710 Silicone Fluid on 40/60 mesh Chromosorb P. Results of representative analyses are summarized in Table II.

Corresponding engine operating parameters are summarized in Table III.

Identification of the numbered peaks in Table II is tabulated in Table IV.

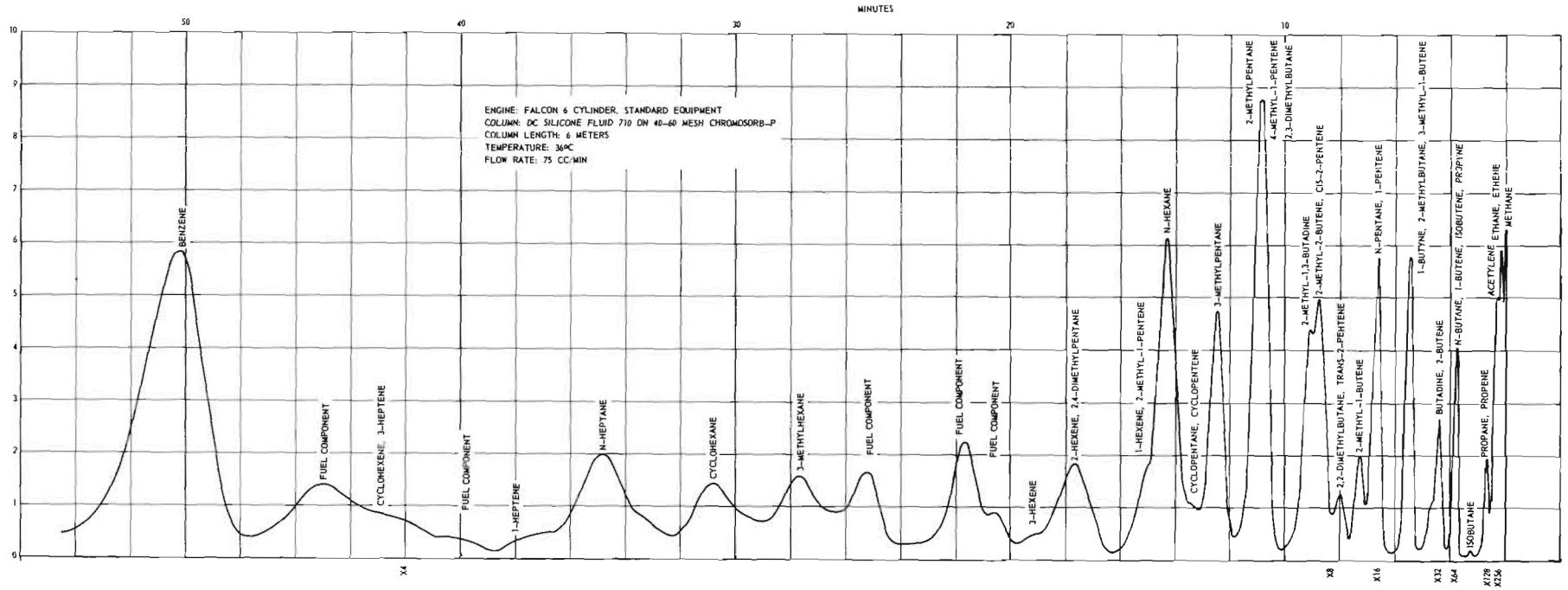


Figure 13. Gas Chromatogram of Medium Boiling Compounds.

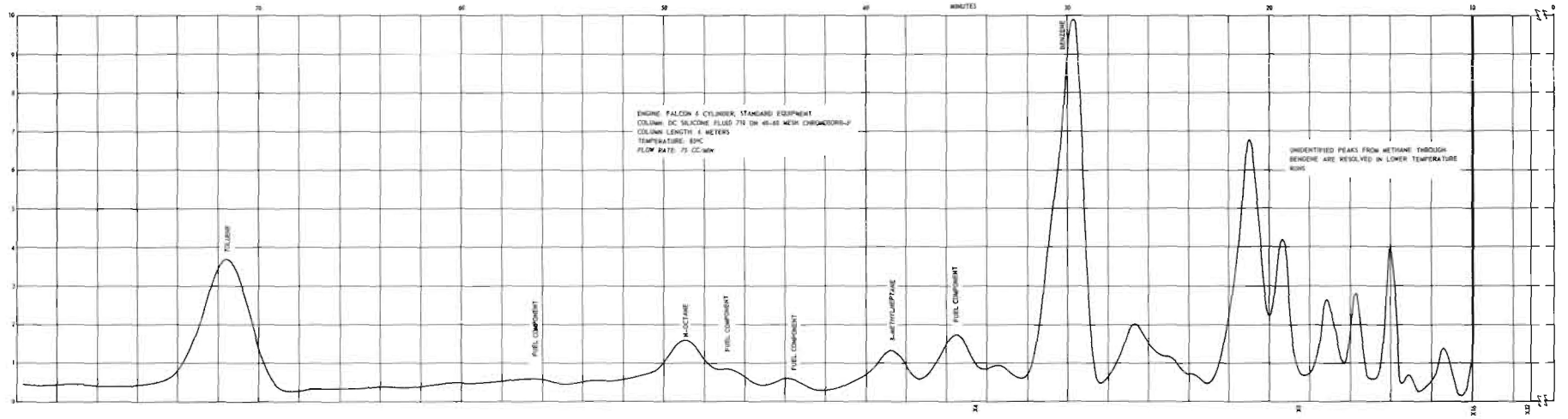


Figure 14. Gas Chromatogram of Medium Boiling Compounds.

TABLE II

MEDIUM BOILING COMPOUNDS IN ENGINE EXHAUST

	a	b	c	d	e	f*	g	h	i	j	k*
0	-	87.5	84.3	17.9	-	-	117.0	-	157.0	-	-
1	27.2	34.0	10.8	7.9	8.1	3.2	23.4	21.2	38.8	27.0	9.5
2	17.5	24.1	8.7	5.6	7.7	2.6	21.6	22.5	33.8	22.7	7.4
3	21.2	20.6	13.1	3.1	4.9	2.5	16.8	24.4	27.0	14.3	6.9
4	12.3	13.3	4.0	3.2	2.8	1.1	8.2	6.6	18.8	11.7	4.3
5	1.9	1.0	1.0	1.0	0.1	0.1	1.0	1.0	0.1	1.0	1.0
6	9.6	10.6	3.0	2.5	2.4	1.4	7.6	12.4	19.3	9.4	3.2
7	40.2	52.0	23.1	14.3	20.0	12.4	7.0	30.8	138.0	54.7	15.9
8	12.4	11.7	3.4	1.9	1.0	1.0	4.0	6.0	70.0	35.0	4.5
9	4.1	4.5	2.2	1.6	1.3	1.5	3.5	2.0	9.3	4.7	1.8
10	7.3	5.6	3.6	1.6	2.6	3.1	4.8	4.8	13.7	8.6	2.8
11	1.0	2.8	1.2	1.5	0.5	1.4	1.0	1.0	5.0	3.0	1.0
12	1.0	9.1	1.0	1.2	1.0	1.0	1.0	1.0	5.0	3.3	1.3
13	6.7	15.2	8.5	4.0	2.8	4.5	6.7	8.0	22.8	20.4	9.0
14	4.1	8.4	3.8	3.0	3.1	3.7	4.5	9.6	27.0	8.8	2.2
15	7.8	10.5	8.4	5.3	6.8	8.3	7.5	17.5	37.5	20.0	5.9
16	6.2	16.0	11.2	4.0	10.0	8.1	4.5	11.3	36.0	17.6	18.7
17	6.0	6.1	3.3	2.0	3.9	4.3	2.5	2.0	15.3	8.4	3.2
18	6.0	13.0	7.4	4.5	6.6	8.1	7.0	5.4	30.8	16.3	4.7
19	13.0	25.9	18.5	8.3	14.8	17.1	16.3	11.8	56.6	34.8	8.7
20	15.0	14.8	12.9	2.6	5.8	4.2	30.8	21.5	28.0	15.6	9.0
21	43.0	48.2	43.6	4.5	26.0	23.6	33.2	21.7	95.7	56.3	26.2
22	4.0	4.5	4.5	1.0	1.8	1.4	3.0	2.2	11.3	4.5	2.3
23	59.0	52.6	41.4	10.4	46.5	21.5	78.0	58.0	126.0	106.0	35.0
24	134.0	130.0	98.1	38.9	62.3	28.8	165.0	171.0	310.0	156.0	71.0
Cracked Prod.	186.5	246.5	110.8	63.7	79.6	60.2	125.6	182.1	517.4	270.6	98.1
Unburned fuel components	274.0	288.0	226.4	70.2	163.2	104.7	333.3	291.6	658.4	389.5	156.9
Total hydrocarbons	460.5	534.5	337.2	133.9	242.8	164.9	458.9	473.7	1175.8	660.1	255.0

* Syringe Sample

TABLE III

COMPONENT IDENTIFICATION FOR TABLE II

Peak No.		Peak No.	
1	1-octene	16	unidentified fuel component
2	3-methyl heptane	17	2-methyl butane
3	unidentified fuel component	18	n-pentane
4	2,2,4 trimethyl pentane		pentenes
		19	pentenes
5	3-heptene	20	2-butyne
6	n-heptane	21	butene-1
7	Benzene		3-methyl butene-1
8	mixture of C_7 compounds		butene-2
		22	butene-2
9	mixture of C_7 compounds	23	butanes
10	2,4 dimethyl pentane	24	propane
11	hexene-1		propylene
12	mixture of C_7 compounds		ethane
			ethylene
13	unidentified fuel component		acetylene
14	cis-4-methyl pentene-2		methane
15	4-methyl pentene-1		
	2,3-dimethyl butane		
	2-methyl pentane		

TABLE IV

ENGINE DATA FOR TABLE II

	a	b	c	d	e	f	g	h	i	j	k
Fuel System	Fuel Inj.	Fuel Inj.	Fuel Inj.	Fuel Inj.	Fuel Inj.	Fuel Inj.	Carb.	Carb.	Carb.	Carb.	Carb.
Valves	Std.	Rotary	Rotary	Rotary	Rotary	Rotary	St.	Std.	Race Cam	Race Cam	Race Cam
H.P.	29.6	7.03	7.08	8.03	8.31	9.82	42.79	20	6.18	3.96	26.7
RPM	1500	1500	1500	1000	1000	1020	2000	2000	1000	1500	1250
Specific Fuel Consumption	0.467	0.787	0.786	0.552	0.572	0.552	0.53	0.58	0.736	1.28	0.483
Air/Fuel Ratio	16.2	15.7	13.76	16.95	15.75	18.0	13.87	13.36	14.3	14.4	15.48

TABLE V

RELATIVE ALIPHATIC HYDROCARBON CONTENT IN EXHAUST* n/g

	a	b	c	d	e	f	g	h	i	j	k
Total Hydrocarbons	1.00	1.16	.73	.29	.53	.36	1.00	1.03	2.56	1.44	0.56
Cracked Hydrocarbons	.82	.86	.68	.21	.49	.31	1.00	.87	1.97	1.17	0.47
Sat'd Hydrocarbons	1.51	1.45	.58	.37	.42	.43	1.00	.88	2.50	1.56	.55
Total Olefins	.93	2.58	.91	.45	.65	.93	1.00	2.65	5.82	2.14	.58
Terminal Olefins	1.00	2.80	1.20	1.50	.50	1.40	1.00	1.00	0.50	3.00	1.00
Internally bonded Olefins	.91	1.86	.84	.67	.69	.82	1.00	2.13	6.0	1.95	4.88
Total Unburned fuel Components	1.10	1.96	.88	.51	.63	.48	1.00	1.45	4.12	2.15	.78

* Column g chosen as representative operating condition.

A number of the peaks cited in Table II represent more than one hydrocarbon component. This imperfect resolution was not regarded as a serious handicap, however, as concentration changes of various classes of exhaust products remained evident with changes in the experimental engine conditions. These changes are summarized in Table V.

C. The High Boiling Compounds

1. Column Preparation

Table VI lists ten hydrocarbons which were separated on a on a 6 meter x 1/8" O.D. column packed with 5% diisodecyl phthalate and 5% Bentone 34 on 60-80 mesh Chromosorb W. Comparable quantitative responses but somewhat poorer resolution were obtained with 4 and 6 meter column prepared as described in Section C-2 and using various combinations of the materials cited. Where more than one liquid phase was used, the materials were dissolved and well mixed before addition to the solid support.

2. Standardization

The detector response was standardized by using dilute solutions of the high boiling compounds in a low boiling solvent. Day by day variations in detector response were estimated by comparison with the response from a 10 ppm propane standard.

3. Results

The exhaust components from the standard carburetor engine are indicated in Figure 15. The chromatogram shown represents a single high temperature separation in the Model 810 gas chromatograph. Lower boiling components were resolved using more efficient columns and suitable oven

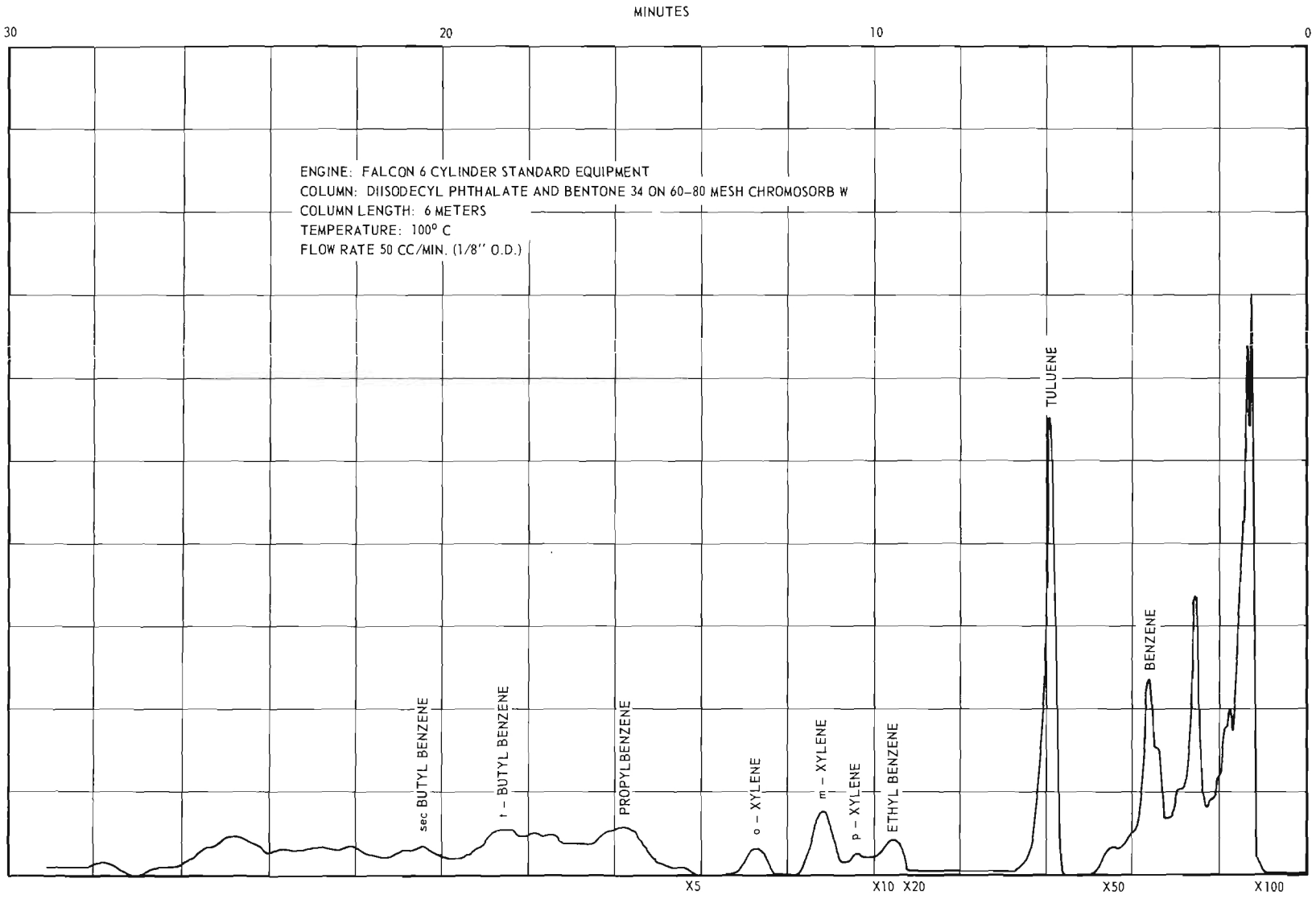


Figure 15. Gas Chromatogram of High Boiling Compounds.

TABLE VI

AROMATIC COMPOUNDS IN ENGINE EXHAUST

	a	b	c	d	e	f
Benzene	13	13	13	37	66	47
Toluene	28	41	44	49	230	107
Ethyl benzene	3	2	3	2	11	9
p-Xylene	1	-	2	< 1	12	7
m-Xylene	3	3	4	2	22	14
Propyl benzene	2	4	3	1	6	6
t-Butyl benzene	2	5	4	1	17	12
sec-Butyl benzene	2	4	3	< 1	8	5
n-Butyl benzene	3	-	-	-	10	7

TABLE VII

ENGINE OPERATING CONDITIONS FOR TABLE VI

	a	b	c	d	e	f
Fuel System	Carb	Carb	Carb	Carb	Carb	Carb
Valves	Std	Std	Std	Std	Std	Std
H.P.	20.5	41.0	28.0	35.0	42.8	20.0
RPM	2000	2000	2000	2000	2000	2000
Specific fuel consumption	0.57	0.48	Unknown	0.52	0.53	0.58
Air/Fuel Ratio	16.25	15.96	Unknown	16.01	13.87	13.36

temperatures in a separate instrument. The unidentified peaks are known to exist in the gasoline, but their large peak width and small area have prevented their identification with known standard hydrocarbons.

The aromatic compounds were separated on a 6 meter 1/8" O.D. column packed with 5 per cent Bentone 34 and 5 per cent diisodecyl phthalate on 60/80 mesh Chromosorb W. As the experimental engine was operated only in a standard conformation during the part of this study where a second gas chromatograph was available, no data on aromatic residues from fuel injection and rotary valve operating modes were obtained. Representative results from experiments with conventional carburetor and standard valves are summarized in Table VI.

Engine operating parameters corresponding to the experiments in Table IV are tabulated in Table VII.

The samples reported in Columns e and f of Table VI were taken from the same engine runs reported in Columns f and g, respectively of Table II.

V. DISCUSSION

The period of research covered in this report was devoted to development of techniques for sampling and analyzing the exhaust gases of the special engine and to examination of the gas samples available. The number and type of samples obtained were sharply restricted by delays in the special engine development project. These delays arose from a number of causes including the experimental nature of the fuel supply and valve systems of the engine and the unexpected death of the scientist in charge of engine development.

A. Analytical Methods

Sampling procedures included freeze-out, gas syringe, Mylar bag, and direct transfer by heated sampling tube and sampling valve. Each of these methods has its advantages and defects; however, the last appears to be the simplest and most accurate. The gas was delivered fresh from the exhaust to the chromatography unit without appreciable change in temperature or opportunity for chemical change to occur. For transfer of samples over greater distances, the heated gas syringe is preferred. For short-term storage of samples the Mylar bag is recommended, although the freeze-out method is more satisfactory for longer term storage.

No single column was most satisfactory. The variations in molecular weight, polarity, degree of saturation, etc., affect the retention times of the various hydrocarbons on the various stationary phases to different degrees. Thus, with one column, two compounds may have virtually equal retention times; their peaks may be easily resolved by another column. A combination of columns serves best to identify all of the components in a mixture as complex as automotive exhaust gas. Also, a column operated at low temperature may resolve the lower molecular weight isomers satisfactorily but be much too slow for the higher molecular weights. Linear temperature programming is one answer to this problem; however, this also has its limitations. It was found preferable to operate two columns simultaneously at different temperatures, as was done in the second period of this study.

The chromatograph curves were evaluated by means of a printing integrator coupled to the recorder; however, this method is satisfactory only in those cases where the peaks are completely resolved. For most of this work it has

been more satisfactory to resort to graphical methods of estimating the areas under peaks. Graphical methods are sufficient if the peak width is large, but introduce large errors if the peak width is small. An equation was derived (see appendix) which excludes peak width from the calculations.

B. Exhaust Compositions

1. Low Boiling Compounds

Variations in the level of low boiling compounds are similar to those observed in the cracked products of the medium boiling range. Since only traces of these compounds have been detected in the fuel, they will be discussed in the following section with the cracked products.

2. Medium Boiling Hydrocarbons

Most of the exhaust residues observed fell in the range of medium boiling fuel components and cracked hydrocarbons. Four modes of engine operation were compared: (a) carburetor with standard valves, (b) carburetor with racing cam, (c) fuel injection with rotary valves, and (d) fuel injection with standard valves. Several trends in exhaust composition were observed to be characteristic of each operating mode. Samples transferred by syringe were lower than those obtained by the sampling valve.

a. Total Hydrocarbons

Total hydrocarbons were highest with the carburetor and racing cam. There appeared to be little difference in the concentration of total hydrocarbon resulting from fuel injection or carburetor feed with standard

valves at similar speeds, air/fuel ratio, and load. A significant decrease in total hydrocarbon was noted with fuel injection and rotary valves. Variation in air/fuel ratio appeared to be of less importance than method of fuel supply and valve characteristics in affecting the level of total exhaust hydrocarbon.

b. Cracked Hydrocarbons

Fuel injection led to lower concentrations of cracked products than were observed with the carburetor. A further decrease in cracked products resulted from use of rotary valves.

c. Saturated Hydrocarbons

Fuel injection with standard valves produced a higher yield of saturated hydrocarbons than did the carburetor, while the application of rotary valves led to a decrease. As with total hydrocarbon and cracked products, the level of saturated hydrocarbon rose sharply with use of a racing cam.

d. Olefins

Olefin concentrations were lower with fuel injection than with carburetor feed. Little change was observed in the concentration of terminal olefins, except that a rise was observed with the racing cam. Fuel injection compares favorably with standard carburetion, while rotary valves produce a further decrease in internally bonded olefins.

e. Total Unburned Fuel Components

A sharp increase in total unburned fuel components arose from use of the racing cam. The level of unburned fuel emission from the racing

cam decreased with increasing engine speed at constant load. The combination of fuel injection and rotary valves produced the lowest observed level of unburned fuel components.

3. High Boiling Compounds

As expected, using carburetor and standard valves, the air/fuel ratio is the factor of greatest importance in determining the level of aromatic hydrocarbon in the exhaust. At equivalent engine speed and air/fuel ratio, increasing load produces an increase in aromatic residues. This rise in aromatic residue with increasing load is more pronounced at low air/fuel ratios.

VI. CONCLUSIONS

1. Significant reduction in the level of hydrocarbon exhaust emission can be obtained by using a well adjusted combination of fuel injection and rotary valves.

2. Under similar conditions of engine speed and air/fuel ratio, the level of unburned fuel components rises with increasing load.

3. Fuel injection leads to a slight decrease in the concentration of cracked hydrocarbons in the exhaust.

VII. APPENDICES

A. Quantitative Analysis

1. Peak areas are assumed to vary in direct proportion to weight of hydrocarbon. There is no assumption that a relationship exists among various hydrocarbons.

2. Four methods have been used to approximate the peak area. Each calculation is based on a standard compound so that relative errors tend to cancel.

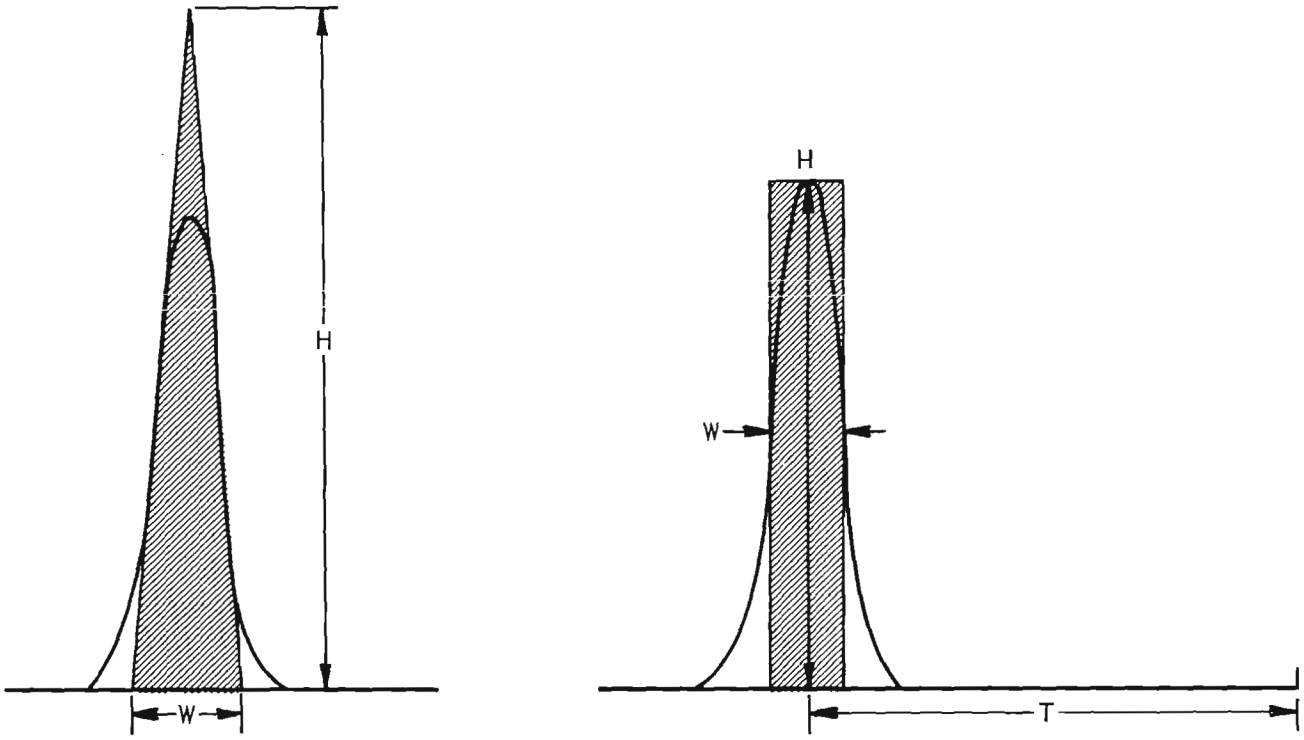
a. The printing integrator is used with a high degree of accuracy only when complete peak separation is obtained.

b. The area of a triangle formed by the intersection of tangents drawn on each side of the peak and the base line (see Figure 15a) provides an approximation of the peak area. $A = 1/2\ WH$. The error becomes greater if the peak is very sharp or assymmetrical.

c. The area of a rectangle with a width equal to the peak width at mid-height and a height equal to the peak height, (see Figure 15b) produces another approximation of the area. $A = WH$.

d. From Figure 15 and the original assumption, an expression is derived giving peak area as a function of peak height and retention time. The result does not actually equal the peak area in all cases but it does provide a reproducible number which is directly proportional to the hydrocarbon weight. Original assumption:

$$\frac{A_1}{M_1} = \frac{A_2}{M_2}$$



Lines are drawn at the tangent intercepts.
W and H are the width and height of the triangle respectively.
Response = 1/2 WH

"W" is the width at one half the height.
"T" is the time interval from the injection point to the peak.
"H" is the height of the peak.
Response = WH

Figure 16. Graphical Methods for Determining Detector Response.

where A_1 = Area of the unknown peak

A_2 = Area of the standard peak

M_1 = Weight of the unknown sample

M_2 = Weight of the standard sample

It follows that

$$\frac{H_1 W_1}{M_1} \simeq \frac{H_2 W_2}{M_2}$$

where W_1 = Width of the unknown peak

W_2 = Width of the standard peak

H_1 = Height of the unknown peak

H_2 = Height of the standard peak

It is desirable to exclude peak width from the equation because of the inaccuracy in measuring small distances (assuming that W_1 and W_2 are not equal). However, the ratio of the peak widths is approximately equal to the ratio of the retention times.

Therefore,

$$\frac{W_1}{W_2} \simeq \frac{T_1}{T_2}$$

where T_1 = Retention time of the unknown peak

T_2 = Retention time of the standard peak

Substituting for $\frac{W_1}{W_2}$,

$$\frac{H_1 T_1}{M_1} \simeq \frac{H_2 T_2}{M_2}$$

$$M_1 \simeq \frac{M_2 T_1 H_1}{H_2 T_2}$$

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